

Diphenyl-beta-Naphthylmethyl and the Color of Free Radicals.

A Contribution to the Chemistry of
Free Radicals

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By

Frederick William Sullivan, Jr.

EASTON, PA.
ESCHENBACH PRINTING COMPANY
1921

*Diss. Ann Arbor
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ACKNOWLEDGMENT

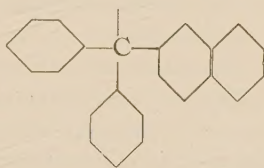
It is a pleasant duty to express my sincere appreciation of the inspiring supervision and interest of Professor M. Gomberg, at whose suggestion and under whose direction this work was carried out.

FREDERICK WILLIAM SULLIVAN, JR.

Ann Arbor, Mich.
August 23, 1922

DIPHENYL-BETA-NAPHTHYL-METHYL AND THE COLOR OF FREE RADICALS

Our purpose in the present investigation has been to prepare the free radical, diphenyl- β -naphthylmethyl



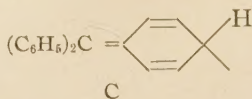
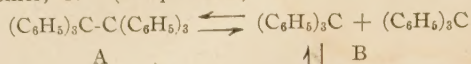
and to study it with regard to the characteristic chemical reactions and physical properties of free radicals; as a later development, because of the peculiar adaptability of this radical to the problem, it was studied especially from the standpoint of the relation between color and chemical constitution. The characteristic phenomena investigated included the absorption of oxygen, the reaction with iodine, the effects produced by light and acids, the conductivity, the dissociation of the hexa-aryl ethane, the formation of additive compounds, and finally, the effect of dilution and temperature changes upon the color of solutions of the free radical.

The striking fact that triphenylmethyl, although a hydrocarbon, is colored when in solution has given rise to many explanations in order to account for this phenomenon. The principal theories regarding the re-

lation between color and constitution of triphenylmethyl are, briefly stated, the following.

1. Colorless hexaphenylethane dissociates to form the colored free radical,¹
 $R_3CCR_3 \longrightarrow 2 R_3C\cdot$

2. Dissociation occurs and is followed by tautomerization of the benzenoid triphenylmethyl into the quinonoid monomolecular tautomer. The color is attributed to the quinonoid tautomer, C.² (Cf. p. 1832.)



The work on *p*-halogen substitution products of triphenylmethyl provides definite, strictly chemical, evidence for the existence of tautomerism with the formation of some kind of a quinonoid tautomer.³

The evidence based on purely physical chemical considerations is somewhat contradictory. Schmidlin observed that upon shaking a solution of triphenylmethyl with oxygen the color vanishes but reappears on standing, and that this phenomenon takes place several times before the solution is completely and permanently decolorized. By weighing the amount of peroxide formed in a single decolorization, he was able to calculate the amount of the colored form which was present. His results indicated that the ratio of colorless to colored form was about 10 to 1. However, since the molecular weight of triphenylmethyl at room temperature corresponds to the dimolecular formula, Schmidlin concluded that color must be due to tautomerism and not dissociation.

Schmidlin also observed the variation in the intensity of color of triphenylmethyl solutions at different temperatures and found that at the freezing point of chloroform, -63° , the color entirely disappeared. Later⁴ he determined the molecular weight of triphenylmethyl in benzene in an apparatus devised to permit the determination by the freezing-point and boiling-point methods on the same sample, and found no changes in dissociation at the different temperatures. He then conducted colorimetric determinations over a range of temperatures from the freezing point to the boiling point of benzene and found that the color increased 6-fold. From these results he concluded that the intensification of color of triphenyl-

¹ Baeyer, *Ber.*, **35**, 1195 (1902). Flurscheim, *J. prakt. Chem.*, **71**, 505 (1905). Chichibabin, *Ber.*, **40**, 3970 (1907). Wieland, *ibid.*, **42**, 3029 (1909). Piccard, *Ann.*, **381**, 347 (1911).

² Gomberg, *Ber.*, **46**, 228 (1913).

³ Gomberg and others, *ibid.*, **39**, 3294 (1906); *ibid.*, **40**, 1886 (1907); *Ann.*, **370**, 181 (1909); *ibid.*, **376**, 208 (1910); *J. Am. Chem. Soc.*, **33**, 538 (1911).

⁴ Schmidlin, *Ber.*, **45**, 3181 (1912).

methyl solutions with rise of temperature must be due to something other than dissociation.

On the other hand, Wieland, Schlenk and Mair, and Piccard took the very opposite point of view. Wieland⁵ concluded from Schmidlin's earlier experiments and from the molecular weight determinations of Gomberg and Cone that, after allowing for the inherent errors of the cryoscopic method, the dissociation hypothesis completely explains color formation.

Schlenk and Mair⁶ gave as evidence that the increase of color with rising temperature is due to dissociation, the results of their molecular weight determinations on triphenylmethyl by the boiling-point method. They found, contrary to Schmidlin, that hexaphenylethane in boiling benzene is dissociated to the extent of 25%. Hence, according to them the increase in color intensity is due to dissociation.

What seemed to be the most convincing evidence in favor of the dissociation theory is found in the work of Piccard⁷ on the increase of color of triphenylmethyl solutions with dilution. This behavior constitutes a deviation from Beer's law, which states that the color absorption of solutions should remain constant if there were no chemical changes on dilution. In the case of hexaphenylethane we are concerned with one of two phenomena, either tautomerism or dissociation. If it were tautomerism the equilibrium would be between two isomers and, Piccard assumes, such an equilibrium should be independent of dilution; but if it were dissociation then the equilibrium would be between a polymer and the products of its dissociation, and such an equilibrium should be influenced by dilution. He conducted a series of experiments on hexaphenylethane solutions and found a decided increase in color upon dilution. He therefore concluded that the phenomenon must be dissociation.

Although Piccard's assumption is in accordance with the general belief⁸ that the equilibrium between tautomers is independent of dilution there is much experimental evidence to the contrary. W. Wislicenus⁹ found that the equilibrium between the aldo and enol forms of ethyl formyl phenyl acetate was shifted in favor of the enol form by concentration. Kurt H. Meyer and Kappelmeier¹⁰ found that the equilibrium between the enol and keto forms of aceto-acetic ester in hexane varied from a concentration of 9.3% enol in a 90% solution of the ester to 58.6% in a 2% solution.

⁵ Wieland, Ref. 2.

⁶ Schlenk and Mair, *Ann.*, **394**, 178 (1912).

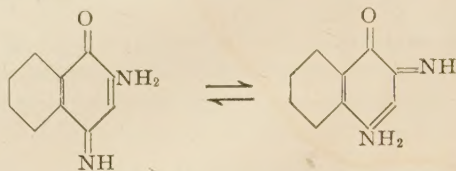
⁷ Piccard, *ibid.*, **381**, 347 (1911); *Arch. sci. phys. Nat.*, Geneva, **1913**, 368. Hantzsch *Ann.*, **384**, 135 (1911); *ibid.*, **398**, 379 (1913).

⁸ Ostwald, "Lehrbuch der Allgemeine Chemie," Wilhelm Englemann 2nd ed., 1902, p. 604.

⁹ Wislicenus, *Ann.*, **291**, 147 (1896).

¹⁰ Meyer and Kappelmeier, *Ber.*, **44**, 2722 (1911).

More recently, O. Miller¹¹ studied the equilibrium between the two forms of 2-amino- α -naphthoquinone-imide and found that this equilibrium was influenced by dilution.



So it seems, after all, that Piccard's results do not prove that color in triphenylmethyl solutions is necessarily due to dissociation, and the possibility remains that it may be due to tautomerism, or perhaps to dissociation with subsequent tautomerism.

The difficulties in the study of this question and the contradictory nature of the conclusions results from the fact that hexaphenylethane is very slightly dissociated, not more than 5% at ordinary temperatures, and therefore conclusions regarding the relation between color and dissociation must be based largely on speculation. Its color is neither sufficiently intense nor sufficiently different from that of its decomposition products for reliable colorimetric study. In diphenyl- β -naphthylmethyl we have a substance of very considerable and accurately measurable dissociation; its color, bright red in concentrated solutions shading to light yellow in dilute solutions, lends itself readily to colorimetric study; it is quite stable towards light; it is readily soluble in a variety of solvents throughout a wide range of temperature. In addition, it shows striking diminution of color within the temperature range of ordinary cryoscopic determinations. On account of this fortuitous combination of properties, a study of diphenyl- β -naphthylmethyl was undertaken in an effort to throw some light on the relation between color formation and changes in concentration and in temperature.

Experimental

Diphenyl- β -naphthyl Carbinol, $(C_6H_5)_2(\beta-C_{10}H_7)COH$.—Diphenyl- β -naphthyl carbinol was prepared by the Grignard reaction from ethyl β -naphthoate and phenylmagnesium bromide. Experiments showed this method to be preferable to the preparation from β -naphthylphenyl ketone and bromobenzene, or from benzophenone and β -bromonaphthalene. The starting substance in the preparation was the sodium salt of β -naphthalene sulfonic acid which was converted to the nitrile by dry distillation with potassium ferrocyanide.¹² Two parts of the sulfonate and one part of anhydrous ferrocyanide were heated in 250g. portions in Pyrex Kjeldahl flasks placed horizontally in an air-bath so that the vapors were removed as fast as formed. The condensate was dried by heating until the water was driven off and was then distilled. The portion boiling between 290° and 310° was collected. The nitrile can be crystallized from petroleum

¹¹ Miller, *J. Russ. Phys. Chem. Soc.*, **47**, 1544 (1915).

¹² Eckstrand, *J. prakt. Chem.*, **38**, 139 (1888).

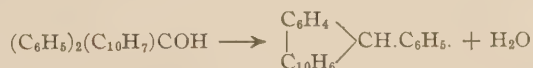
ether and melts at 68°. The redistilled substance was hydrolyzed according to the procedure of Baeyer and Besemfelder¹³ and the resulting acid purified by dissolving in alkali and reprecipitating with acid. In this manner 650 g. of acid was prepared from 3900 g. of the sulfonate, a yield of 20%.

For the esterification of the acid, 20 g. of β -naphthoic acid, 20 g. of sulfuric acid and 200 cc. of absolute alcohol were boiled under a reflux condenser. The reaction product was poured into an excess of dil. alkali, the ester was extracted from this mixture, dried and distilled, and the fraction between 300° and 304° was collected. The yield of ester was 97.5%. When the proportions were changed to 1 part of β -naphthoic acid, 1 part of sulfuric acid, and 2 parts, instead of 10, of alcohol, the yield of the ester was reduced, but, since the unchanged acid could be recovered, this latter method was adopted.

Ullmann¹⁴ found that the product of the reaction between methyl- β -naphthoate and phenylmagnesium bromide was an oil and he was unable to isolate the carbinol from it. Following the same procedure and using either the methyl or ethyl ester we were able to obtain the crystalline carbinol but the yield was not more than 25%. The yield was improved by replacing the ether after the formation of the Grignard reagent by benzene or, better, by toluene. Xylene was not so satisfactory. The following procedure was finally adopted. A mixture of 10 g. of magnesium turnings in 50 cc. of bromobenzene and 200 cc. of ether was boiled until the metal disappeared; 100 cc. of toluene was then added and the ether was distilled; 28 g. of ethyl β -naphthoate was then added gradually; the heat of the reaction kept the toluene boiling, and the temperature of the reaction mixture was about 115°. After the ester had been added and when boiling had ceased, the mixture was cooled and decomposed with ice and acetic acid. The product was distilled with steam and the residue was taken up in carbon disulfide. The solution was dried, filtered and concentrated. On the addition of petroleum ether, a light-yellow crystalline product, the carbinol, separated and this was suitable for conversion to the chloride without further purification; yield, 28 g., or 65%. The carbinol is readily soluble in all the usual solvents and can be recrystallized from alcohol or, better, from carbon disulfide, by the addition of petroleum ether. The pure, white, recrystallized product melts at 117.5°.

Analyses. Calc. for $C_{23}H_{18}O$: C, 89.0; H, 5.84. Found: C, 89.4, 89.4; H, 5.90, 5.92.

When boiled with acetic acid in the presence of mineral acids, the carbinol is converted to the fluorene.



This substance, when recrystallized from chloroform by the addition of alcohol, melts at 137° and agrees in all properties with the substance described by Ullmann.

Diphenyl- β -naphthylmethane, $(C_6H_5)_2(\beta-C_{10}H_7)CH$.—Ten g. of the carbinol is dissolved in 200 cc. of acetic acid and the solution is boiled with 20 g. of zinc dust until a drop no longer gives a red color with sulfuric acid. The acetic acid solution is poured into water and partly neutralized. The ether extract is washed with alkali, dried and concentrated. The hydrocarbon crystallizes on the addition of alcohol; yield, 9 g., or 95%; m. p., 77–78°.

Analysis. Calc. for $C_{23}H_{18}$: C, 93.83; H, 6.17. Found: C, 93.44; H, 6.33. Mol. wt. Calc.: 294. Found: 293.

¹³ Baeyer and Besemfelder, *Ann.*, **266**, 188 (1891).

¹⁴ Ullmann, *Ber.*, **38**, 2218 (1905).

The properties of diphenyl- β -naphthylmethane as here described differ from those which appear in the chemical literature and which are based on the work of Lehne.¹⁵

Diphenyl- β -naphthylmethyl Chloride, $(C_6H_5)_2(\beta-C_{10}H_7)CCl$.—The chloride is prepared by saturating an ether solution of the carbinol with hydrogen chloride in the presence of calcium chloride. After standing, the solution is decanted, boneblack is added and the ether is evaporated. The oily residue is taken up in low-boiling petroleum ether, filtered and allowed to crystallize. The recrystallized substance melts at 94.5° , and the yield is practically quantitative. The use of acetyl chloride instead of hydrogen chloride in this preparation leads to the formation of colored impurities, and is not recommended.

Analysis. Calc. for $C_{23}H_{17}Cl$: Cl, 10.79. Found: 10.71.

The chloride gives red additive compounds with stannic and mercuric chlorides. When dissolved in alcohol or, preferably, in an alcoholic solution of sodium ethylate, the chloride is converted to diphenyl- β -naphthylmethyl ethyl ether, $(C_6H_5)_2(\beta-C_{10}H_7)-COC_2H_5$, a colorless crystalline substance which melts at 114° . The chloride gives an anilide, $(C_6H_5)_2(\beta-C_{10}H_7).C.NH.C_6H_5$, melting at 158.5° .

Diphenyl- β -naphthylmethyl Bromide, $(C_6H_5)_2(\beta-C_{10}H_7)CBr$.—The bromide can be prepared by the addition of acetyl bromide to a benzene solution of the carbinol. After recrystallizing from petroleum ether it is colorless and melts at 136° . On long standing it turns red with the evolution of acid fumes.

Analysis. Calc. for $C_{23}H_{17}Br$: Br, 21.4. Found: 21.6.

Preparation of Diphenyl- β -naphthylmethyl.—Five g. of diphenyl- β -naphthylmethyl chloride and 5 g. of molecular silver are placed in a test-tube and 35 cc. of carbon disulfide is added. The tube is then corked, taking all the necessary precautions, and shaken for several hours.^{16,17} When the reaction is complete, the bright red solution is siphoned into the free-radical apparatus. The apparatus is immersed in warm water, suction is applied and the solvent is completely evaporated. Five cc. of acetone is added, the oily residue is dissolved and the apparatus is filled with carbon dioxide. The solution is cooled to a temperature below 0° ; crystals of the free radical separate after standing for 2 to 3 days. The solvent is drawn off and the crystals washed with acetone, then dried under reduced pressure in a stream of carbon dioxide; 2.5 to 3 g. of pure white or light yellow, finely divided, crystalline powder, the triarylmethyl, is thus obtained. The compound is very soluble in all the usual solvents except petroleum ether. It melts in an atmosphere of carbon dioxide between 135° and 140° to a reddish liquid. The dry substance is quite stable at ordinary temperatures and may be exposed to air for short periods without danger of oxidation.

Calc. for $C_{23}H_{17}$: C, 94.16; H, 5.84. Found: C, 93.92; H, 6.02.

Formation of Additive Compounds with Solvents.—Owing to its extreme solubility, it is very difficult to crystallize diphenyl- β -naphthylmethyl and the crystallization always requires from 2 to 3 days. The

¹⁵ Lehne, *Ber.*, **13**, 358 (1880).

¹⁶ Gomberg and Schoepfle, *J. Am. Chem. Soc.*, **39**, 1659 (1917).

¹⁷ Gomberg and Cone, *Ber.*, **37**, 2034 (1904).

ketones are, as a class, best suited as solvents for recrystallization, although it is possible to recrystallize the free radical from a few solvents of other classes. In order to determine whether additive compounds were formed with different solvents, the procedure already given for the recrystallization of the substance from acetone was used with the substitution in each case of the solvent whose additive tendency was to be investigated. In case the solvent was one of high boiling point, the free radical after recrystallization was freed from the non-volatile solvent by washing with a little low-boiling petroleum ether. The solid substance was dried thoroughly under reduced pressure at room temperature. A weighed sample of the dry free radical was then placed in a porcelain boat and heated at 70° under reduced pressure in an atmosphere of carbon dioxide. The free radical was recrystallized from the following solvents and separated without solvent of crystallization: (I) ketones: acetone, methylethyl ketone, methylhexyl ketone, dipropyl ketone; (II) ethers: diethyl ether, ethyl *iso*-amyl ether; (III) esters: ethyl acetate.

With methylbutyl ketone, diphenyl- β -naphthylmethyl gives an additive compound in which the proportion of ketone to free radical approaches that required in accordance with the general formula of such compounds with triphenylmethyl, $R_3C-CR_3.C_6H_{12}O$. Three samples, 1.020, 1.526 and 0.481 g. showed 0.073, 0.175 and 0.050 g. loss or 7.1, 11.8 and 10.4%, respectively, whereas the calculated loss is 14.6%.

Among other solvents which were tried but from which the free radical failed to crystallize altogether were benzene, benzonitrile, caprylene and cyclohexane.

Reaction with Oxygen.—Diphenyl- β -naphthylmethyl rapidly combines with the amount of oxygen necessary for the formation of the peroxide in accordance with the equation, $2(C_{23}H_{17}) + O_2 \longrightarrow (C_{23}H_{17})O-O(C_{23}H_{17})$. The apparatus for the measurement of the oxygen absorption¹⁸ consists of an absorption bottle which is connected by a heavy rubber tube to a gas buret. To determine the oxygen absorption, a weighed quantity of diphenyl- β -naphthylmethyl chloride and an equal weight of silver were placed in a tube, bromobenzene was added and the tube was sealed and shaken for several hours. The tube containing the reaction mixture was placed in bromobenzene in the absorption bottle, the apparatus was sealed, exhausted and filled with oxygen. When the system had come to equilibrium, the tube was broken by shaking the bottle. Shaking was continued until the color of the free radical had permanently disappeared and the reading was taken half an hour later. The oxygen absorbed by the previously isolated, crystalline, free radical was also determined and, of course, silver was left out. The following table gives the results of typical experiments.

¹⁸ Ref. 17, p. 1661.

TABLE I

REACTION WITH OXYGEN

	Weight of sample		Oxygen absorption	
	$C_{23}H_{17}Cl$ G.	$C_{23}H_{17}$ G.	Cc. at Stand. Cond.	% of Calc.
1	1.200	...	40.8	99.6
2	1.200	...	41.6	102
3	1.200	...	41.0	100
4	...	1.029	39.3	100
5	...	1.000	39.0	102

Peroxide.—The yield of peroxide varies greatly under different conditions. When an ether solution of the free radical is oxidized with air the yield is 72%, while the use of benzene as a solvent reduces the yield to 46%. The peroxide when recrystallized from benzene is pure white and melts at 166°.

Analyses. Calc. for $C_{46}H_{34}O_2$: C, 89.3; H, 5.54. Found: C, 89.3, 89.6; H, 5.54, 5.50.

Action of Light and of Acids.—The free radical is not very sensitive to light. A 5% solution in bromobenzene which was exposed to full daylight during three days in December still absorbed 75% of the calculated amount of oxygen. When a 10% solution of the free radical in bromobenzene was treated with an equal volume of bromobenzene saturated with hydrogen chloride, the color of the free radical rapidly disappeared and the solution, after 3 hours, absorbed no oxygen.¹⁹

Action of Iodine.—Diphenyl- β -naphthylmethyl reacts with iodine in accordance with the following equation, $2(C_6H_5)_2(\beta-C_{10}H_7)C + I_2 \longrightarrow 2(C_6H_5)_2(\beta-C_{10}H_5)CI$ but an equilibrium is reached before the reaction has gone to completion. A weighed sample of the free radical in benzene was titrated with a 0.1 *N* solution of iodine in benzene. The color of the iodine disappeared rapidly until 70% of the calculated amount was added, then the absorption of iodine ceased. The change from the color of the free radical to the color produced by excess of iodine can be readily detected. Three samples of 1.000 g. each required 23.0, 23.7 and 25.0 cc. of 0.1 *N* iodine solution, or 67.5, 70.0 and 73.5% of the calculated amount, respectively.

The presence of the iodide in solution was demonstrated by its conversion to the anilide, which substance proved to be identical with diphenyl- β -naphthylmethyl anilide prepared from the corresponding chloride.

The Conductivity.—For the determination of the conductivity a cell resembling the one used in the earlier work²⁰ was used. It differed from the other in that the electrodes were placed horizontally instead of vertically. The cell constant was determined using a 0.02 *N* potassium

¹⁹ Ref. 17, p. 1663.

²⁰ Gomberg and Cone, *Ber.*, **38**, 1342 (1905).

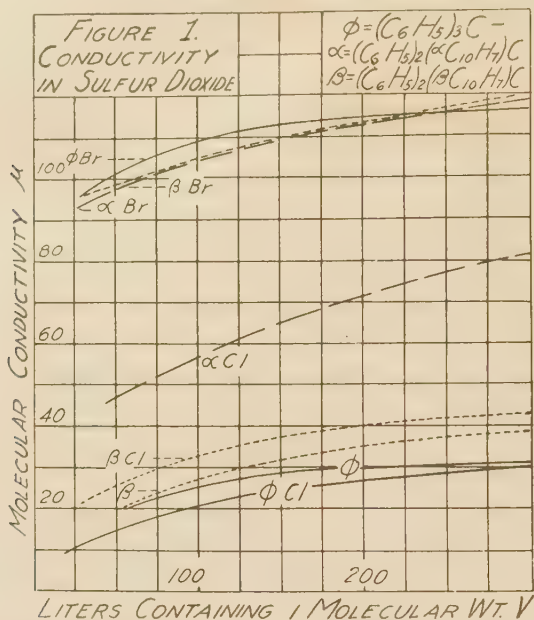
chloride solution at 25°. The sulfur dioxide was passed through a tube of phosphorus pentoxide 50 cm. long, and was then condensed in the cell, which was surrounded by a freezing mixture. The cell was then stoppered and placed in a Dewar flask which contained liquid sulfur dioxide. By such a procedure it was possible to maintain in the surrounding bath a constant temperature of -8° , the boiling point of liquid sulfur dioxide. It was found that the cell could be removed from the cooling solution long enough to weigh it without generating too much pressure. After weighing, the cell was connected into the usual Wheatstone bridge apparatus, and the conductivity of the pure solvent was determined. In all experiments, the conductivity of the solvent was between 10^{-5} and 10^{-6} mhos. The material whose conductivity was to be determined was introduced in 3 portions. The cell was shaken after each addition until all the substance was dissolved, as indicated by the fact that the reading had become constant. Determinations were made of the conductivity of triphenylmethyl and of its chloride and bromide at -8° , with the cell immersed in liquid sulfur dioxide, and at 0° in a mixture of ice and water. The conductivities of diphenyl- α -naphthylmethyl chloride and bromide, and those of diphenyl- β -naphthylmethyl chloride and bromide were determined at -8° only.

Contrasting with its behavior in other solvents, diphenyl- β -naphthylmethyl was found to be quite insoluble in sulfur dioxide. For this reason the substance was dissolved in toluene and measured quantities of this solution were added to sulfur dioxide. The same procedure was carried out with triphenylmethyl and it was found that in both cases the re-

TABLE II
CONDUCTIVITIES IN SULFUR DIOXIDE

$(C_6H_5)_3CCl$				$(C_6H_5)_3CBr$			$(C_6H_5)_2(\alpha-C_{10}H_7)-$ CCl		$(C_6H_5)_2(\alpha-C_{10}H_7)-$ CBr	
	V	μ_{-8}	μ_o	V	μ_{-8}	μ_o	V	μ_{-8}	V	μ_{-8}
1	154	24.2	20.2	237	113	118	2600	128	1180	138
2	43.7	14.0	11.3	112	108	112	179	70	223	118
3	18.2	9.1	7.8	39.6	97.6	99.5	59.4	50	55.7	102
1	205	27.9	23.1	189	117	122	1271	117	683	124
2	61.0	16.6	13.4	60.7	105	107	334	84.6	184	108
3	26.3	11.5	9.2	28.2	96.4	97.9	46.9	44.8	46.7	95.6
$(C_6H_5)_3C-$ in SO_2 + C_7H_8				$(C_6H_5)_2(\beta-C_{10}H_7)C-$ in SO_2 + C_7H_8			$(C_6H_5)_2(\beta-C_{10}H_7)CCl$		$(C_6H_5)_2(\beta-C_{10}H_7)CBr$	
	V	μ_{-8}	% C_7H_8 by Vol.	V	μ_{-8}	% C_7H_8 by Vol.	V	μ_{-8}	V	μ_{-8}
1	211	31.4	2.62	227	34	2.57	1072	73.8	692	131
2	108	26.3	5.11	116	27.1	5.02	212	41.4	148	110
3	57	20.2	9.72	60.2	22.0	9.57	30.5	20.1	25.9	96.5
1	195	28.6	2.81	261	39.4	2.24		...	892	129
2	100	26.6	5.47	133	31.4	4.39	283	42.2	325	123
3	52.9	19.5	10.4	68.4	22.5	8.41	27.1	23.2	27.4	96.6

sulting solutions of the mixed solvents were good conductors, much better than a solution of triphenylmethyl in sulfur dioxide alone. The readings were taken 1 hour after the additions were made. The accompanying tables and curves show the results of these experiments.



Conductivity in Hydrocyanic Acid.—The same apparatus was used as in the determination of the conductivities in sulfur dioxide. The hydrocyanic acid was generated by the addition of a concentrated solution of sodium cyanide to a 50% solution of sulfuric acid and the gas evolved was dried by calcium chloride and phosphorus pentoxide. It was then condensed in the conductivity cell. The specific conductivity of the hydrocyanic acid was never greater than 10^{-5} mhos.

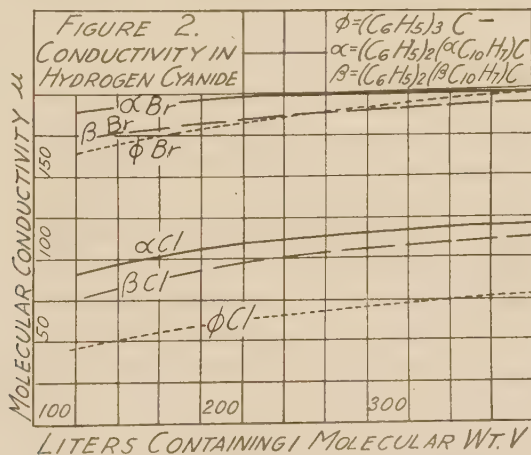
It was found that the conductivity of the triarylmethyl halides in hydrocyanic acid did not remain constant, but changed gradually. For this reason it was not possible to determine the conductivity by dissolving the solid substance in this solvent. Experiments showed that the conductivity of triphenylchloromethane in hydrocyanic acid to which 15% of benzene was added, was not greatly affected by the further addition of benzene up to 20%. It was found that benzene and hydrocyanic acid mixed without a change in volume. It was, therefore, decided to add the halides dissolved in benzene to hydrocyanic acid; 22 cc. of the solvent was condensed in the cell and 3 cc. of benzene was added. To this mixture was added, first, 0.07 cc. of benzene containing the substance whose conductivity was to be determined, second, 0.23 cc. more and, finally, 0.7

cc., a total of 1 cc. of solution. The readings were taken 5 minutes after each addition and the series of three readings was always completed in 15 minutes. The conductivities were all determined at 0° using an ice-bath. The density of hydrocyanic acid at this temperature is 0.7112.

TABLE III
CONDUCTIVITY IN HYDROCYANIC ACID

$(C_6H_5)_3CCl$		$(C_6H_5)_3CBr$		$(\alpha-C_{10}H_7)(C_6H_5)_2CCl$	
V	μ_o	V	μ_o	V	μ_o
1659	111	1790	211	1794	161
391	77	420	206	422	117
121	44	130	166	130	77
1668	115	1726	212	1704	170
393	75	406	202	424	118
121	45	125	165	131	76
$(\alpha-C_{10}H_7)(C_6H_5)_2CBr$		$(\beta-C_{10}H_7)(C_6H_5)_2CCl$		$(\beta-C_{10}H_7)(C_6H_5)_2CBr$	
V	μ_o	V	μ_o	V	μ_o
1830	200	1690	166	1767	216
416	197	404	125	382	203
129	174	125	86	127	191
1740	192	1711	166	1704	193
409	198	404	122	401	206
126	174	125	85	124	191

The conductivities of the chlorides and bromides of triphenylmethyl, diphenyl- α -naphthylmethyl and diphenyl- β -naphthylmethyl were determined in hydrocyanic acid. Unfortunately the conductivities of the free radicals themselves could not be determined because when a benzene solution of a free radical is added to hydrocyanic acid an amorphous precipitate is formed and the solvent remains colorless and nonconducting.



Molecular Weight.—The molecular weight of diphenyl- β -naphthylmethyl was determined in 8 solvents, covering a temperature range of

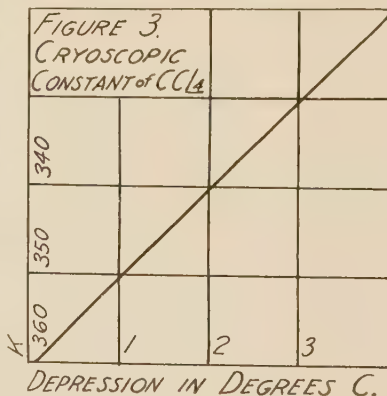
from -22° to 80° . The standard Beckmann apparatus with electromagnetic stirrer was used. Details for the manipulation for solvents freezing above 0° have been previously published.²¹ The determination of the molecular weight in solvents freezing at low temperatures is described below. A large number of solvents were tried out, including benzonitrile, dimethyl resorcin, ethylene chlorohydrin and *o*-nitrotoluene but all these were discarded because of supercooling; aniline was found unsuitable because of the insolubility of the free radical in it. The solvents finally chosen were carbon tetrachloride, m. p. -22° , and ethylene chlorobromide whose freezing point, -17° , had been determined by Schneider.²²

The apparatus used consisted of the usual freezing-point tube which was passed through a rubber stopper into a Dewar flask in which ether could be evaporated under reduced pressure, and this served as the bath. A thermometer, a tube leading to the suction pump and a tube for the introduction of ether were also passed through the same stopper. A description of the procedure for the determination of the cryoscopic constant of carbon tetrachloride will give a typical illustration of the use of the apparatus.

The freezing-point tube containing the thermometer, stirrer and a weighed quantity of solvent was placed in the Dewar flask. Ether was introduced into the latter until the lower portion of the tube was immersed. The stirrer was then set in motion and suction was applied. The rapid evaporation of the ether surrounding the freezing-point tube reduced the temperature, and freezing occurred with very little supercooling. After each reading the crystals were melted, and five readings were taken for each freezing point. Three additions of the solute were made. Duplicate determinations of the constant were made with triphenylmethane and benzophenone as the solutes.

As will be seen from the accompanying curve, when this procedure was followed the value of the so-called freezing-point constant varied with the depression in carbon tetrachloride. For this reason it was thought advisable to use the values obtained from this curve for K when calculating the molecular weight of the free radical. Beckmann used this solvent for freezing-point determinations, but did not encounter this difficulty.²³

Ethylene chlorobromide was made according to Simpson's²⁴ method by



²¹ Ref. 17, p. 1662.

²² Schneider, *Z. physik. Chem.*, **22**, 232 (1897).

²³ Beckmann, *Z. anorg. Chem.*, **67**, 31 (1910).

²⁴ Simpson, *Proc. Roy. Soc.*, **27**, 118 (1878). Delepine and Ville, *Bull. Soc. Chim.*, [4] **27**, 673 (1920).

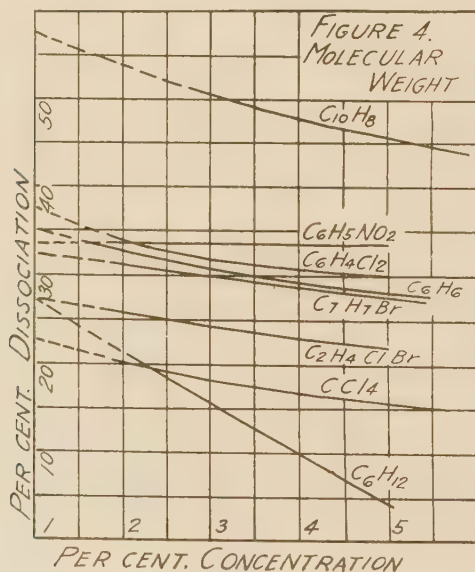
passing ethylene into a mixture of chlorine, bromine and water. The freezing-point constant was determined according to the method described for carbon tetrachloride, using triphenylmethane and benzophenone. Since the values obtained in this case were constant, the average of the determinations was used. Ethylene chlorobromide possesses unusual advantages as a cryoscopic solvent. It has a high constant and super-cools only very slightly. As far as we know, it is the only suitable solvent freezing at or near -17° .

The determinations of the molecular weight of the free radical were carried out in an atmosphere of hydrogen. Three additions were made and the resulting concentrations were from 1% to 5%. The samples were all dried under reduced pressure in an atmosphere of carbon dioxide. In no case was the same sample used for two determinations, but new material, prepared on the day the determination was made, was used each time. The following solvents were used: carbon tetrachloride, ethylene chlorobromide, benzene, nitrobenzene, cyclohexane, *p*-bromotoluene, *p*-dichlorobenzene and naphthalene. In the experiments using naphthalene, where it was possible that the high temperature might produce decomposition, repeated determinations showed that the freezing point remained perfectly constant and, therefore, the conclusion is justified that no decomposition was taking place.

TABLE IV
MOLECULAR WEIGHT

Solvent	Constant <i>K</i>	Weight of solvent G.	Weight of solute G.	Concen- tration %	Depres- sion $^{\circ}$ C.	Molec- ular wt.	Disso- ciation %
CCl_4	348	25.41	0.4620	1.84	1.284	498	17.7
M. p. -22°	333		1.0567	4.20	2.785	503	61.5
	324		1.4716	5.86	3.673	518	13.1
	345	25.44	0.5614	2.21	1.588	580	21.8
	335		0.9963	3.92	2.606	503	16.5
	321		1.5700	6.17	3.978	501	16.9
$\text{C}_2\text{H}_4\text{ClBr}$	86.3	25.03	0.5349	2.14	0.393	469	25.0
M. p. -17°			0.9527	3.81	0.695	471	24.4
			1.2783	5.11	0.916	480	22.1
		25.08	0.4627	1.70	0.342	464	26.3
			0.9450	3.77	0.676	480	22.1
			1.2533	5.01	0.896	481	21.8
C_6H_6	52.0	17.69	0.3697	2.09	0.248	438	33.8
M. p. 5.3°			0.6612	3.74	0.430	452	29.6
			1.1352	6.42	0.720	463	27.2
		20.05	0.3447	1.72	0.201	443	32.3
			0.5704	2.85	0.337	442	32.6
			0.9163	4.57	0.540	461	27.1
$\text{C}_6\text{H}_5\text{NO}_2$	69.0	20.06	0.4028	2.01	0.316	438	33.8
M. p. 5.7°			0.7298	3.64	0.573	438	33.8
			0.9735	4.95	0.779	439	33.5

		20.10	0.3597	1.79	0.280	441	32.9
			0.7425	3.69	0.571	446	31.4
			0.9772	4.86	0.762	440	33.2
C_6H_{12}	200	20.05	0.4855	2.42	0.972	498	17.7
M. p. 5.8°			0.7828	3.90	1.482	527	11.2
			0.9824	4.90	1.735	565	3.7
		20.02	0.4271	2.13	0.908	481	21.8
			0.7191	3.59	1.388	518	13.1
			1.0211	5.1	1.832	557	5.2
$CH_3C_6H_4Br$	85.5	27.66	0.4879	1.76	0.333	451	30.6
M. p. 27°			0.9900	3.58	0.668	456	28.5
			1.4848	5.37	0.988	462	26.8
		27.41	0.5239	1.91	0.365	445	32.1
			1.0770	3.93	0.740	451	30.0
			1.5160	5.53	1.024	459	27.7
$C_6H_4Cl_2$	72.2	24.91	0.5223	2.10	0.342	444	32.0
M. p. 53°			1.0577	4.25	0.682	451	30.0
			1.5200	6.10	0.974	454	29.1
		25.11	0.4940	1.97	0.330	431	36.0
			0.9472	3.77	0.604	451	30.0
			1.4246	5.86	0.914	448	30.8
$C_{10}H_8$	71	19.97	0.5615	2.81	0.515	388	51.0
M. p. 80°			0.9633	4.84	0.854	402	45.8
			1.1818	5.92	1.029	408	43.6
		19.50	0.5381	2.76	0.499	391	49.9
			0.9548	4.90	0.856	400	46.5



The Quantitative Determination of the Number of Decolorizations Produced by the Action of Oxygen on Solutions of Diphenyl- β -Naphthylmethyl.—The fact that solutions of free radicals are decolorized by

shaking with oxygen and that the color reappears upon standing has been referred to in the introductory part of this paper. The approximate number of such decolorizations has been determined by several investigators.²⁵ We found that such results varied greatly with the conditions of the experiment. Therefore, a definite procedure was adopted and an apparatus was devised for the investigation of this phenomenon. The apparatus was quite similar to the usual form of absorption apparatus which has already been described, except that the absorption vessel was replaced by a 100cc. Nessler tube. This tube was tightly stoppered and provided with a fairly close fitting cork piston which was moved by an iron rod passing through the stopper. In order to make a gas-tight joint, yet one through which the rod would slide easily, an iron tube slightly larger than the rod was inserted in the stopper and a rubber tube was fitted tightly over both the iron sleeve and the rod. By the use of a little glycerine this joint was made perfectly gas tight and yet it did not hinder the free motion of the piston. A tube connecting with the gas buret was also inserted through the rubber stopper.

For the determination, a 1g. sample of the free radical was placed in a test-tube of 15cc. capacity, sufficient bromobenzene was added to fill the tube, and the tube was sealed. The substance was quickly dissolved by shaking. The tube was then placed in the Nessler tube just described, enough bromobenzene was added to make a total volume of 50 cc. and the tube was connected with the buret of the absorption apparatus. The apparatus was exhausted and filled with oxygen. The test-tube was broken by pressing down the piston, which was adjusted so that its under surface was in contact with the surface of the liquid, thus sealing the solution almost completely from the oxygen above. The liquid in the gas buret was leveled and the reading was taken. The piston was then withdrawn as far as possible in order to admit a fresh supply of oxygen and the solution was shaken for a few seconds until the color of the free radical disappeared. The piston was then quickly pushed in and the absorption was determined. The same procedure was repeated at 2-minute intervals. After the last easily perceptible color change had taken place, the tube was shaken vigorously until no more absorption of oxygen occurred. The last reading represents not merely the oxygen required to produce perceptible decolorization but the amount necessary to complete entirely the oxidation of the free radical. The values for the percentage of oxygen absorbed at each interval are based, not on the amount which would be required by theory for the entire oxidation, but on the actual amount of oxygen which was absorbed in the experiment under consideration. This hap-

²⁵ Schmidlin, *Ber.*, **41**, 2476 (1908). Schlenk and Weickel, *Ann.*, **372**, 7 (1909). Schlenk and Renning, *ibid.*, **394**, 194 (1912). Schmidlin and Garcia-Banus, *Ber.*, **45**, 3186 (1912).

pened to be somewhat less than that calculated for the amount of free radical taken.

TABLE V
DECOLORIZATION BY OXYGEN

Sample I				Sample II		
Weight of sample, 1.000 g.				Weight of sample, 1.000 g.		
Solvent, 50 cc. of C_6H_5Br				Solvent, 50 cc. of C_6H_5Br		
Temp., 21°. Bar., 744 mm.				Temp., 22°. Bar., 730 mm.		
% of calc. absorption, 87.3				% of calc. absorption, 96.7		
Interval	Total ^a oxygen ab- sorption	Oxygen ^a abs. for single decolorization	% of total absorp- tion	Total ^a oxygen absorption	Oxygen ^a abs. for single decolorization	% of total absorp- tion
1	5.1	5.1	14.9	5.2	5.2	13.9
2	9.2	4.1	26.7	8.9	3.7	24.0
3	12.9	3.7	37.5	13.2	4.3	35.6
4	16.9	4.0	49.0	17.3	3.9	64.9
5	19.6	2.7	56.9	19.9	2.6	53.9
6	22.3	2.7	64.7	22.6	2.7	61.1
7	23.8	1.5	68.9	25.3	2.7	68.3
8	25.6	1.8	74.2	27.6	2.3	74.5
9	26.7	1.1	77.3	29.2	1.6	78.9
10	28.0	1.3	81.2	30.8	1.6	83.2
Total	34.5	6.5	100	37	6.2	100

^a Corrected to standard conditions.

Similar experiments were conducted with triphenylmethyl and diphenyl- α -naphthylmethyl but the turbidity produced by the immediate precipitation of the peroxide obscured the end-point. Twelve clearly distinguishable changes were observed with the former and only three with the latter. Such a method as here employed is suited for use only with compounds which show a decided color change on oxidation and which give a clear solution by virtue of the solubility of the corresponding peroxide, as happened to be the case with diphenyl- β -naphthylmethyl.

Colorimeter for the Study of the Changes in Intensity of Color of Solutions of Free Radicals.—For the quantitative determination of the color of a free radical solution of a Campbell-Hurley colorimeter²⁶ was used, with such changes as were necessary in order to work in the absence of oxygen.

The tube, *B*, which was to contain the solution under investigation was fitted with a glass plate sealed to the top and with 2 side-arms placed near the top. The lower side-arm was fitted with a ground-glass joint to which was attached a 3-way stopcock, *a*. One opening of the stopcock connected with a funnel for the introduction of solvent while the other led to the carbon dioxide generator. The upper side-arm was connected through a stopcock, *b*, to the suction pump. The other colorimeter tube, *A*, which was to contain the standard solution, was also sealed with a plate at the top and fitted with 2 side-arms, one as near the bottom as possible and the other near the top. The

²⁶ Campbell and Hurley, *J. Am. Chem. Soc.*, **33**, 1112 (1911).

lower arm was connected by a ground-glass joint to a tube leading to the Drechsel bottle, *C*, which served as a reservoir for the standard solution. To the other arm of the Drechsel bottle was fused a 3-way stopcock, *c*, one arm of which connected with the suction pump and the other with the carbon dioxide generator. This arm of the Drechsel bottle was attached also to a second 3-way stopcock, *d*, one outlet of which connected with the funnel for the introduction of solvent and the other led back to the upper side-arm of the colorimeter. This upper side-arm was also fitted with a 2-way stopcock, *e*, and trap for the outlet of carbon dioxide. The carbon dioxide for these experiments was freed from all traces of oxygen by passing over reduced copper at a dull red heat.

To prepare the standard solution, 0.5 g. of the free radical was placed in the Drechsel bottle, *C*. The apparatus was evacuated, filled with carbon dioxide and 100 cc. of benzene was added. The free radical dissolved

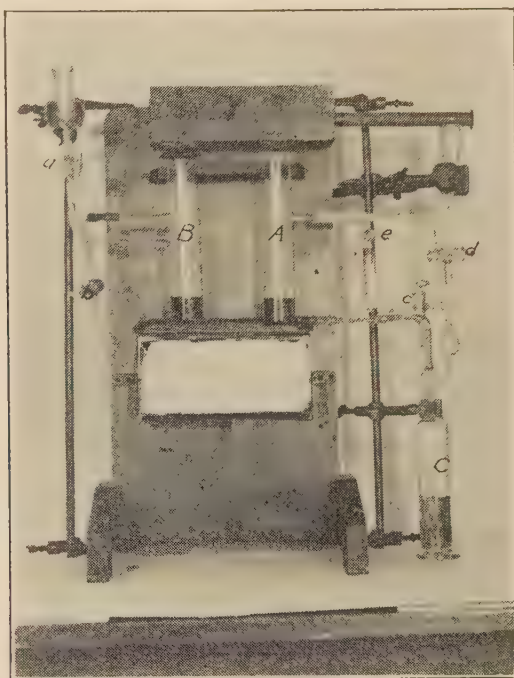


Fig. 5.

rapidly. The apparatus was kept under a positive pressure of carbon dioxide all the time. To raise the column in the colorimeter tube, the stopcock *d* was closed and the stopcock *e* was opened. The pressure forced the solution into the colorimeter tube. To empty the colorimeter tube the stopcock *d* was opened and *e* was closed. By repeating this procedure a few times, the solute was completely dissolved and the solution was well mixed. The reliability of the apparatus was thoroughly tested. A solution in *B* when made up to the same strength as the standard in *A*

and compared with it was invariably balanced exactly by a column of the standard solution of the same height.

The Effect of Dilution on the Color of Solutions of Free Radical in Benzene, Nitrobenzene and Cyclohexane at their Respective Freezing Points.—(One-quarter g. of the free radical was dissolved in 5 cc. of solvent in the colorimeter tube *B*. The solution was frozen by immersing in a cooling mixture and then allowed to melt until a few crystals remained. It was then compared with the standard in *A* and 5 readings were taken. Readings were easily duplicated within 1 mm.* The solution was then diluted by the addition of 5 cc. of solvent, frozen and compared with the standard again. Finally it was diluted to 25 cc. This procedure was carried out with each of the 3 solvents. The experiments were carried out in duplicate on solutions made by dissolving different samples of free radicals, but since the two experiments checked exactly only one is reported.

TABLE VI
CHANGE OF COLOR WITH DILUTION

Read- ings	Volume soln. Cc.	Nitrobenzene		Benzene		Cyclohexane	
		% Conc. by wt.	Height standard Mm.	% Conc. by wt.	Height standard. Mm.	% Conc. by wt.	Height standard. Mm.
1	5	4.15	13	5.68	11.5	6.85	10
2	10	2.08	17	2.84	16	3.43	14
3	25	.83	25	1.14	23	1.37	19

The Effect of Temperature on the Color of Solutions of the Free Radical in Carbon Tetrachloride and in Toluene.—A solution containing 2 g. of the free radical per 100 cc. of carbon tetrachloride was frozen in a mixture of carbon dioxide and toluene. The color at the freezing point was compared with that of the standard solution at room temperature. A number of comparisons were made throughout a temperature range from the freezing point of carbon tetrachloride, -22° , to $+30^{\circ}$. Similar com-

TABLE VII
CHANGE OF COLOR WITH TEMPERATURE

Height of solution, 17 mm.			
Temp. CCl_4 $^{\circ}\text{C.}$	Height stand. Mm.	Temp. C_7H_8 $^{\circ}\text{C.}$	Height stand. Mm.
..	..	-39	3
..	..	-26	4
-22	6	-18	6
-15	8	-10	9
..	..	-5	11
0	15	0	13
..	..	5	17.5
10	23	12	20.5
20	33	20	28
..	..	25	35
30	50	30	41

parisons were made upon a 2% toluene solution at various temperatures, from the freezing point of mercury, -39° , to $+30^{\circ}$. The standard solution for these comparisons was, as before, a 0.5% solution of the free radical in benzene.

The fact that the color of the free radical solution upon cooling does not decrease beyond a certain limit, may be due to the presence of colored impurities. This suspicion is strengthened by the fact that the solid free radical itself is colored slightly. If this surmise be correct, then the readings given are all somewhat too high and should be corrected by subtracting the value of the least reading, 3 mm. We were unable to obtain a solution of the free radical in carbon tetrachloride or toluene whose color disappeared entirely even when cooled to the lowest temperature obtainable with a mixture of carbon dioxide and toluene.

Discussion of Results

Diphenyl- β -naphthylmethyl is a pure white substance which rapidly becomes yellow on standing, even in an atmosphere of carbon dioxide. In contrast to its α -naphthyl isomer, it is very soluble in all the common solvents and crystallizes only on long standing.

It absorbs the theoretical amount of oxygen to form the peroxide but does not give a high yield of the crystalline substance. The free radical is quickly decomposed by hydrogen chloride and slowly acted on by light.

The equilibrium between the free radical and iodine is reached when 70% of the theoretical amount of iodine has been added. The concentrations of the products present when equilibrium has been reached are intermediate between those in the case of triphenylmethyl and in the case of diphenyl- α -naphthylmethyl.

The results of the conductivity determinations show that the property of electrolytic dissociation is a general one for this class of compounds. The bromides give strongly conducting solutions with but little difference between the conductivities of the individuals. The chlorides are not such good conductors and there is a variation among them. The conductivities of the chlorides are related in the same way as the dissociation of the corresponding free radicals; the chloride of diphenyl- α -naphthylmethyl, highest; of diphenyl- β -naphthylmethyl, next; and of triphenylmethyl, least. Triphenylmethyl chloride has a large negative temperature coefficient of conductivity. The same relation holds for the free radicals themselves; diphenyl- β -naphthylmethyl is a better conductor than triphenylmethyl.

The conductivity of the triarylmethyl halides in hydrocyanic acid is uniformly higher than in sulfur dioxide. The bromides show molecular conductivities comparable to that of an aqueous solution of potassium hydroxide or about twice the conductivity of the alkali halides in water.

This is a striking fact, in view of the high molecular weight, 373, the great complexity of the molecules, and in view of the absence of any basic groups like the amino group. The chlorides conduct less than the corresponding bromides and the individual variations are the same as those observed for the same substances in sulfur dioxide.

The colors of the solutions of the free radicals in sulfur dioxide are: triphenylmethyl, orange yellow; diphenyl- α -naphthylmethyl, green; diphenyl- β -naphthylmethyl, red. The halides of these free radicals give the same colors when dissolved in sulfur dioxide, hydrogen cyanide or sulfuric acid. The color is very intense and a minute quantity of substance suffices to impart a deep color to a large volume of solvent. Merely from a visual comparison of the solutions of diphenyl- β -naphthylmethyl or of its halogen derivatives in sulfur dioxide with a benzene solution of the free radical itself, it is evident that the phenomenon of electrolytic dissociation with the accompanying color is entirely different from the phenomena of dissociation and color formation of the free radical which takes place in non-dissociating solvents. Also, the same difference is apparent when the bright green sulfur dioxide solutions of the α -naphthyl derivatives are compared with the dark brown solution of this free radical in benzene. Kurt H. Meyer and H. Wieland²⁷ had previously come to a similar conclusion in regard to triphenylmethyl and its derivatives. As a result of spectroscopic investigations, they found that the colors of triphenylmethyl solutions in sulfur dioxide and in benzene, while apparently identical, in reality were distinctly different.

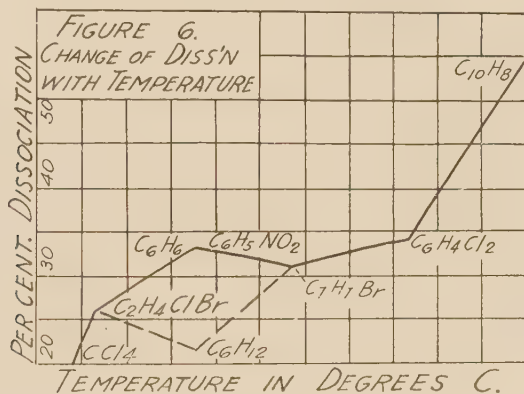
As a result of previous molecular weight determinations upon a number of free radicals certain generalizations have been drawn concerning their dissociation. Diphenyl- β -naphthylmethyl conforms to the generalization that dissociation increases with dilution except in a few cases where deviations can be attributed to experimental errors.

The results of the determinations of the molecular weight of triphenylmethyl indicate that, within certain limits, the dissociation of hexaphenyl ethane is proportional to the temperature of the solution and independent of the nature of the solvent. This hypothesis was borne out by subsequent work on diphenyl- α -naphthylmethyl which showed a very regular increase in dissociation with increase in temperature, quite independent of the nature of the solvent. In a set of experiments upon the β -naphthyl free radical, performed to test this point, using nitrobenzene, benzene and cyclohexane, it was found that there are exceptions to this rule. The solvents all possess approximately the same freezing points, 5° to 6°. In nitrobenzene and benzene, the molecular weights are practically the same. In cyclohexane, however, the molecular weight of the free radical is very high and increases rapidly with concentration until, in a 5% solu-

²⁷ Meyer and Wieland, *Ber.*, **44**, 2557 (1911).

tion, it is almost completely associated. This peculiar behavior is in harmony with the observations of Mascarelli and Benati²⁸ who found that, as compared with the ordinary cryoscopic solvents, cyclohexane was very strongly associating. It might be expected that a solvent possessing this tendency would certainly exhibit it toward a free radical. The accompanying graph shows that, in general, dissociation increases with temperature.

The results of the experiments on the relation between dissociation and the oxygen necessary to produce decolorization proves conclusively that the color is not proportional to the dissociation. A 2% solution of the hexa-aryl ethane in *p*-bromotoluene at its freezing point is about 30% dissociated. A bromobenzene solution of the same concentration at the

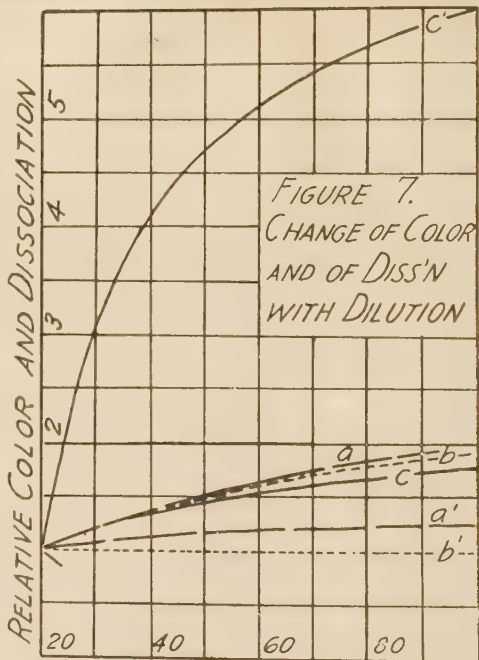


same temperature is completely decolorized by only 14% of the oxygen necessary for complete oxidation. How are we to explain the fact that the decolorization is produced by only $\frac{1}{2}$ of the oxygen which would be necessary to oxidize the whole amount of the monomolecular form present in solution? Evidently only on the assumption that the monomolecular form exists as two tautomers, one of which is colored and which reacts more rapidly with oxygen than the colorless form. Of course, the results obtained by decolorization cannot be assumed to represent the true amount of the colored tautomer, first, because the colorless form may also be absorbing some oxygen and, second, because the colorless form undoubtedly tautomerizes partly into the colored form during the process of decolorization. The values do certainly represent the *maximum* possible amount of the colored tautomer in the solution. These results differ from Schmidlin's on triphenylmethyl in that the decolorization experiments here described are paralleled by a series of accurate molecular-weight determinations on a substance of appreciable dissociation, and we are therefore

²⁸ Mascarelli and Benati, *Gazz. chim. ital.*, **39**, [2] 642 (1909).

in a position actually to correlate intensification of color with increase of dissociation.

It was found that solutions of the free radicals in cyclohexane, benzene and nitrobenzene are of about the same intensity of color and that the intensity of color changes equally in all cases on dilution, in spite of the differences in dissociation in these solvents. Assuming the color of a 5% solution to be unity, we can calculate the relative intensity of color at dilutions down to 1% in reference to this unit. Plotting these color values against the dilution, that is, the number of grams of solvent containing 1 g. of solute, we obtain curves *a*, *b*, *c*, (Fig. 7), showing the relative change of color intensity with dilution. Similarly, we assume the degree of dissociation at 5% as our unit and calculate the relative degree of dissociation at other dilutions with reference to this unit. These values are also plotted against the dilution, and the resulting curves *a'*, *b'*, *c'*, show the relative change in dissociation on dilution. It is apparent, in nitrobenzene and benzene the intensity of color almost doubles with the decrease of concentration from 5% to 1% and yet the change in dissociation throughout the same range is very slight. On the other hand in cyclohexane, the dissociation increases three times as much as the color. This again shows that color is independent of dissociation, that is, an increase in dissociation may occur without an equal increase in color intensity.

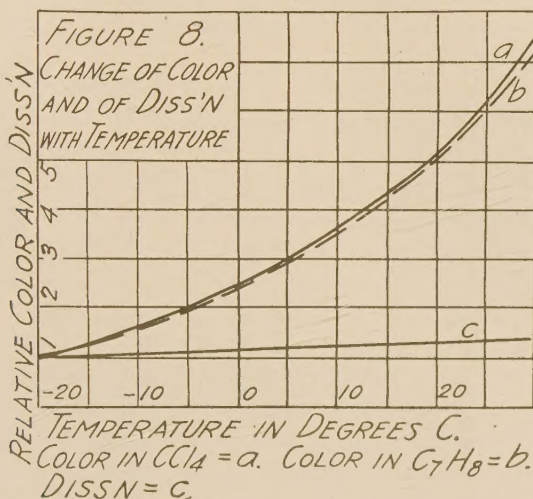


DILUTION = CC. CONTAINING 1
GRAM OF SUBSTANCE

COLOR IN	DISS'N IN
$C_6H_6 = a$	$C_6H_6 = a'$
$C_6H_5NO_2 = b$	$C_6H_5NO_2 = b'$
$C_6H_{12} = c$	$C_6H_{12} = c'$

It was found that a solution of the free radical in carbon tetrachloride at its freezing point, or in toluene at -40° , is only slightly colored although it is dissociated to the extent of from 15 to 20%. On gradually warming these very light colored solutions, an increase in color begins to take place between -30° and -20° and this color increases 10 times with a rise of temperature of 50° while the dissociation increases only $\frac{1}{2}$ with the same

change of temperature. If we assume as the unit of color intensity the color of a solution at -20° and calculate the relative color intensity at other temperatures with reference to this unit, then plot these values against the temperature, we obtain curves *a*, *b*, (Fig. 8), showing the relative increase of color with temperature. If we now take as our unit of dissociation the amount of dissociation at -20° we can calculate the relative dissociation at other temperatures with reference to this unit. Plotting these values against the temperature we obtain a curve, *c*, showing the increase of dissociation with rise of temperature. The accompanying curves show the striking differences between the change in the degree of dissociation and the change in color intensity which occurs when the temperature of the solution of the free radical is varied.



It is not our purpose to explain in what manner the effect of dilution, or that of rising temperature, operates to disturb the equilibrium between the colored and colorless modifications of the free radical. However, our results do definitely prove that changes in color intensity take place independently of changes in dissociation. The evidence presented is convincing. This being so, then the observed facts can best be explained by the assumption that we are dealing here with an equilibrium between benzenoid and quinonoid tautomers of the triaryl methyl,²⁹ and that an increase in the proportion of the quinonoid tautomer is the cause of the increase of color.

Summary

1. Diphenyl- β -naphthyl carbinol has been synthesized from ethyl β -naphthoate and phenylmagnesium bromide. A number of its de-

²⁹ Cf. p. 1811.

rivatives were prepared. Diphenyl- β -naphthylmethyl chloride was obtained by the action of hydrogen chloride on the carbinol. When the chloride was treated with molecular silver, the free radical, diphenyl- β -naphthylmethyl, resulted.

2. The radical was isolated in the crystalline state. A careful study was made of its reactions with oxygen, iodine and acids, and of the effect of light. The conductivity of the free radical, diphenyl- β -naphthylmethyl, was determined in sulfur dioxide. The conductivities of the chlorides and bromides of triphenylmethyl, diphenyl- α -naphthylmethyl and diphenyl- β -naphthylmethyl were determined in both sulfur dioxide and hydrogen cyanide. These compounds, especially the bromides, were found to be good conductors. The molecular weight of diphenyl- β -naphthylmethyl was determined in 8 solvents whose freezing points covered the range from -22° to $+80^{\circ}$. It was found that the hexa-arylethane was dissociated from 15% to 50%.

3. Experiments were carried out to find what effect changes in concentration of the free radical would have upon the dissociation and upon the color of the solutions. It has been found that the resulting changes in color intensity are independent of the changes in dissociation. It has also been found that the changes in color intensity which result from variations in temperature are, again, not parallel to the changes in dissociation which are thus produced. These facts point to the conclusion that color formation in solutions of free radicals is not due wholly to dissociation of the hexa-aryl ethane into the tri-aryl methyl. The most satisfactory explanation of the facts is the hypothesis that in addition to dissociation we have tautomerization of the benzenoid tri-arylmethyl into the quinonoid form. The equilibrium between the dimolecular and monomolecular forms on the one hand and the equilibrium between the two monomolecular tautomers on the other hand, are not equally influenced by changes either in concentration or in temperature.

This investigation was made with the assistance of The National Aniline and Chemical Company Fellowship, and we wish to express our obligations for the generous aid we have thus received.

